In conclusion, we claim to have established that, in the case of an active catalyst where the surface concentration of the adsorbed compound is at a maximum, chemical action takes place at a regular rate so long as an adequate supply of the interacting substances is maintained at the surface. The forces regulating this supply may be physical rather than chemical in nature.

The Origin of the " Cyanogen " Bands.

By S. Barratt.

There are, in addition to the line and the positive and negative band spectra of nitrogen, several other series of bands, in the production of which this element plays some part. The emission centres responsible for these bands have generally been identified with the molecules of compounds of nitrogen with other elements, though these molecules are not necessarily those of compounds which can be isolated under normal circumstances, and possibly may prove to be more of the nature of temporary associations. Such spectra include the so-called third positive band spectrum of nitrogen, the various spectra attributed to ammonia or other nitrogen-oxygen complexes, and also the cyanogen bands.

The NO bands, Deslandres' third positive group of nitrogen bands, are found in vacuum tubes filled with nitrogen, when they contain a trace of oxygen as impurity. They have also been observed in the carbon arc surrounded by a magnesia block,[*] in uncondensed spark discharges in air and nitrogen, and in the flames of cyanogen and ammonia. They were formerly believed to be due to nitrogen alone, but Deslandres, Schniederjost, Lewis and others have proved that their production is dependent upon the presence of oxygen.

The spectra obtained from compounds or mixtures of nitrogen and hydrogen are more complex. What is probably the true ammonia spectrum was discovered by Schuster.[†] It was observed when a continuous stream of ammonia was passed through a vacuum tube, and disappeared immediately upon interruption of the gas flow, presumably owing to complete decomposition of the ammonia. Another spectrum is characterised by a strong

[*] Liveing and Dewar, ‘Roy. Soc. Proc.,’ vol. 34, p. 418 (1882).
[†] ‘Roy. Soc. Proc.,’ vol. 20, p. 484 (1872).

band in the ultra-violet, with a head at λ 3360. It was discovered by Eder*
in the flame of ammonia burning in oxygen.

Lewis† observed the same band in vacuum tubes containing nitrogen and
hydrogen, and found that the presence of both gases was essential for its
production. The band has been observed in the carbon arc by King‡; and
Fowler,§ who has succeeded in identifying this band in the solar spectrum,
mentions its occurrence in the flame of wet cyanogen. Owing to the
persistent appearance of the band in company with the cyanogen bands, it
has frequently been confused with a part of the latter spectrum.‖

The persistence of this band in vacuum tubes filled with ammonia, after
the disappearance of Schuster's spectrum, and its presence in the solar
spectrum, indicate that the centres responsible for the emission of the two
spectra are different.

Judging from its conditions of stability, it is some compound of nitrogen
and hydrogen other than ammonia which is responsible for the band at
λ 3360, and, whilst referring to this band as the "ammonia band," Fowler
expressly recognised that this possibility is not excluded.

The cyanogen bands were originally attributed to a compound of carbon
and nitrogen, as they are characteristic of the flame of burning cyanogen,
and of the carbon arc in nitrogen. Lockyer (1880) claimed that these
bands were as strongly developed in the carbon arc burning in dry chlorine
as in the ordinary arc in air. Later, also, he observed the bands when
a spark discharge was passed through carbon tetrachloride vapour. He
concluded that the bands were part of the Swan spectrum, nitrogen not
being essential for their production. This theory was contested by Liveing
and Dewar,¶ who found that the bands could not be developed under the
conditions imposed by Lockyer, if the last traces of nitrogen were rigorously
excluded, and showed, in fact, that the appearance of the bands was an
exceedingly delicate test for the presence of nitrogen in any form.

Foley** observed that the intensity of the cyanogen bands from the
carbon arc is by no means proportional to the amount of nitrogen present.
He stated that the intensity of the bands from the arc in cyanogen is little
greater than from that in air, and, further, that the intensity is not much
diminished by replacing the air by carbon dioxide. He inclined to the

    * 'Denkschr. Wien. Akad.,' vol. 60, p. 1 (1893).
    † 'Astrophys. Journ.,' vol. 40, p. 154 (1914).
    ‡ 'Astrophys. Journ.,' vol. 14, p. 323 (1901).
    § 'Phil. Trans.,' A, vol. 218, p. 351 (1919).
    ‖ *Cf.* King, *loc. cit.*, and Kayser, 'Handbuch der Spectroscopie,' vol. 5, p. 229.
    ¶ 'Roy. Soc. Proc.,' 1880.
    ** 'Phys. Rev.,' vol. 5, p. 149 (1897).

view that the cyanogen bands are due to carbon in the presence of nitrogen, but not combined with it.

It was generally conceded, however, that the bands only appeared under conditions ensuring the presence of both nitrogen and carbon, until the question was re-opened in 1914, by Grotrian and Runge.* Their conclusions, which have been widely accepted† were to the effect that the cyanogen bands were due to nitrogen alone.

The experimental basis for this statement was derived from a study of the conditions under which the spectrum may be observed in the Schonherr elongated arc. This type of discharge has some advantages over the ordinary arc for spectroscopic work. Grotrian and Runge claim that the spectra due to the electrode materials are only visible in the immediate neighbourhood of the electrodes themselves; all impurities, also, are swept away by the current of gas necessary to preserve the stability of the arc. If this be so, the spectrum emitted from the central part of the arc will depend only upon the nature of the gas passing through it. The cyanogen bands were found under these conditions, with nitrogen, prepared in the usual manner from liquid air, streaming through the arc. Their intensity was unaffected by the composition of the electrodes, for which copper, iron, platinum, magnesium, aluminium, and carbon were successively used. No other bands usually attributed to carbon were detected; and, finally, the intensity of the bands remained unaltered after the introduction of varying proportions of carbon dioxide. The conclusion drawn from these observations was that carbon is not essential for the production of the cyanogen bands. The absence of the bands from the spectra of metallic arcs in air, which would appear to militate against this view, Grotrian and Runge explained by an inhibiting effect of oxygen upon their development. Their appearance in the carbon arc was held to be due to the removal of the atmospheric oxygen as carbon oxides.

In illustration, they quote an experiment with an arc between copper electrodes. In nitrogen containing a little oxygen, this arc did not show the cyanogen bands, but these appeared when the nitrogen entering the chamber had previously been passed through pyrogallol.

Hemsalech, recently‡ stated in a footnote that as a result of his own experiments he was unable to endorse these views; and, indeed, added that he has obtained indications that the presence of nitrogen is not always essential for the emission of the bands.

* 'Phys. Zeitschr.,' vol. 15, p. 545.

† *Cf.* Stähler, 'Handbuch der Arbeitsmethoden,' vol. 2, i, 497 ; and St. John 'Astrophys. Journ.,' vol. 46, p. 251 (1917).

‡ 'Phil. Mag.,' vol. 39, p. 256 (1920).

The experiments described in this paper originated with an observation of the peculiar appearance of the coal-gas nitrous oxide flame, which suggested the possibility of detecting a spectrum peculiar to the latter gas. Though no indications of a new spectrum were detected in the various flames examined, the results proved to be of some interest in relation to the origin of the cyanogen bands.

As a preliminary, the spectrum obtained by streaming nitrous oxide through a vacuum tube was studied, after the method introduced by Schuster for ammonia. The inlet of the vacuum tube was fused to a long and fine capillary, which regulated the rate of inflow of the gas; and the outlet of the tube was attached to a mechanically driven air-pump. The nitrous oxide was taken from a cylinder supplied for medical use. The green " after-glow " of the gases leaving the path of discharge was stronger in nitrous oxide than in air.

Photographs were taken of the discharges in the capillary of the vacuum tube when nitrous oxide and air, successively, were allowed to pass through the tube. No new bands appeared in the nitrous oxide discharge, but several bands, also visible with air, were considerably intensified with respect to the rest of the spectrum. These were measured by means of a comparison spectrum and included a diffuse band in the yellow, stretching from $\lambda = 5992$ to 5969, and three bands of about $\lambda = 5517$, 5407, and 5397 A.

The remaining observations were made upon the spectra of various flames. The burner used with these flames was a small brass hand blowpipe, of a type in which the gases were thoroughly mixed before reaching the jet. The axis of the flame was arranged vertically in front of the slit of the spectograph, and the light was focussed upon the slit by a quartz lens. This arrangement permits the analysis of the light from the various cones of a flame. A Hilger quartz spectrograph was used, with a dispersion of 35 A. per millimetre at $\lambda = 4000$ A. It was provided with a wave-length scale which could be photographed on the plate, in juxtaposition to the flame spectrum, and which was of great assistance for the purpose of identification.

The nitrous oxide was taken direct from a cylinder, and as it was of the purity exacted for medical purposes, it was considered to require no further purification. The hydrogen was also taken from a cylinder, and the preparation of the other gases is described below.

Nitrous Oxide—Coal-Gas Flame.

The structure of this flame is complex, as it possesses at least five zones The innermost, and brightest, is yellow and is brilliantly luminous at its apex. The greenish yellow mantle is common to all the flames obtained with

nitrous oxide and appears to be a general feature of all flames in air in which nitrogen compounds are burnt. In presence of a large proportion of nitrous oxide, just before the flame becomes unstable, the inner cones shrink into a single small cone, which is purple in tint. No new bands were found in the spectrum of the flame. The spectrum of the inner cone, photographed as has been described, contained the following groups :—

The Swan bands with heads at $\lambda\, 5164$, $\lambda\, 4736$, and $\lambda\, 4381$.

The CH bands with heads at $\lambda\, 4315$.

The OH bands with heads at $\lambda\, 2811$ and $\lambda\, 3063$.

The CN bands with heads at $\lambda\, 4600$, $\lambda\, 4216$, $\lambda\, 3883$, and $\lambda\, 3590$.

The NH band with a head at $\lambda\, 3360$.

The hydrocarbon bands (Eder's Cη band)* from $\lambda\, 4048$ to $\lambda\, 3872$.

All these were strongly developed.

Nitrous Oxide—Hydrogen Flame.

The strong development of the cyanogen bands in the nitrous oxide coal-gas flame suggested a method by which Grotrian and Runge's conclusions as to the origin of the cyanogen bands might be put to the test. If the bands are emitted by nitrogen, as they claim, independently of the presence of carbon (except as a reducing agent, as in the carbon arc), then the appearance of the bands in the flame just described must be attributed to the nitrous oxide alone, and should be unaffected by the substitution of hydrogen for the coal-gas as a constituent of the flame. The nitrous oxide-hydrogen flame was accordingly photographed. In structure the flame resembles that obtained with coal-gas, but its spectrum is more simple. The water vapour and the " ammonia " bands were very strong, but the Swan spectrum, the CH band, and the bands attributed to hydrocarbons were all absent. As the cyanogen bands in the first photograph taken were practically as intense as they had been in the coal-gas flame, it was thought that confirmation of Grotrian and Runge's theory had been obtained. Eventually, however, the appearance of the bands was traced to the use of rubber gas connections which had been employed in the experiments with coal-gas. When these were replaced by fresh pieces of tubing which had been treated for some time with boiling water, the photograph showed only a trace of the cyanogen head at $\lambda\, 3883$, and this was so weak that it could only be detected on very close examination of the plate. The intensity of the " ammonia " band, on the other hand, was unaffected.

In a subsequent experiment it was found possible, by further precautions, to obtain a plate showing no trace of the cyanogen bands. The burner was

* Eder and Valenta, ' Denkschr. Wien Akad.,' vol. 67, p. 483 (1899).

thoroughly cleaned with acid, and steam was blown through it for a considerable time. The length of rubber tubing actually coming into contact with the gases was reduced to a minimum, and, as a further precaution, both gases were passed through long glass tubes packed with solid caustic soda, to remove carbon dioxide. Under these conditions the last trace of the head at λ 3883 disappeared, though a slightly longer exposure was given than in the previous experiments. It would thus appear that atmospheric carbon dioxide is unable to cause the production of the cyanogen bands in the inner cone of such a flame. Both the band at λ 3360 and the water vapour bands were present with unaltered intensity. These observations appear to leave no doubt that the presence of carbon is essential for the emission of the cyanogen bands in flames. If the bands were due to nitrogen, the introduction of the volume of hydrocarbon that could escape from a short length of rubber tubing, after passage of a considerable volume of hydrogen beforehand, should not have affected appreciably their intensity. Actually the presence of this trace of hydrocarbon resulted in the strong development of all the cyanogen bands ; while, when the contaminated tubing was removed, the head of the strongest band could barely be detected, and when further precautions were taken to ensure the elimination of carbon, even this persistent head at λ 3883 also disappeared.

It is evident that the cyanogen bands constitute a more delicate test for the presence of carbon in flames than do the remaining carbon bands, and that the cyanogen band at λ 3883 persists in the presence of extremely minute quantities of carbon.

Carbon Monoxide—Nitrous Oxide Flame.

This flame was thought to be worth investigating, as it contains no hydrogen. If the origin of the "ammonia" band is a nitrogen-hydrogen molecule, its production should not be possible when the presence of hydrogen in the burning gases is excluded. The carbon monoxide was prepared by the action of concentrated sulphuric acid upon formic acid. It was stored over dilute alkali, and was passed, previous to combustion, over solid caustic soda, soda lime, and calcium chloride. The flame resembles in structure that of carbon monoxide burning alone in air, but is white, instead of having the familiar blue colour. It has the usual yellow-green mantle, which has been mentioned above. The spectrum contained only the "continuous" band of burning carbon monoxide with, faintly superimposed upon it, the water vapour bands at λ 2811 and λ 3063. There was no indication of either the cyanogen, or the "ammonia" bands. The absence of the latter band is confirmatory evidence for the view that the presence of hydrogen is essential for its

emission. The appearance of the OH bands is to be attributed to atmospheric water vapour.

Carbon Monoxide—Nitric Oxide Flame.

This flame was examined in order to confirm the observations made with the corresponding nitrous oxide flame. The nitric oxide was prepared in the usual manner from a mixture of sodium nitrate and ferrous sulphate, by the action of concentrated sulphuric acid.

The appearance and spectra of the two flames were identical, and the cyanogen bands and the " ammonia " bands were again absent.

The absence of the cyanogen bands from both these flames is interesting. The fact that they were not developed appears to indicate that the chemical reactions in these flames are unfavourable to the production of the carbon-nitrogen compound responsible for the cyanogen bands, a circumstance which is not *a priori* improbable, when it is borne in mind that the carbon present is already partially oxidised, and would tend to pass into carbon dioxide directly in the process of combustion.

Carbon Monoxide—Ammonia Flame.

The absence of the cyanogen bands from the CO—N_2O, and CO—NO flames suggested the examination of a carbon monoxide flame fed with ammonia, in place of an oxide of nitrogen; for in this case the reducing action of the ammonia on the carbon monoxide might reasonably be expected to favour the probability of the formation of cyanogen. The carbon monoxide was charged with ammonia before reaching the jet by passage over the surface of a concentrated aqueous solution of ammonia. The flame presented the characteristic yellow coloration of flames which contain ammonia, and the water vapour and the ammonia band at λ 3360 were well developed, while the cyanogen band at λ 3883 was faintly visible. The "continuous" carbon monoxide spectrum was also present.

This broad band of burning carbon monoxide has generally been considered truly continuous, but in all the photographs obtained during these experiments, it appeared to be distinctly banded. Between wave-lengths $\lambda = 5000$–3000 A the spectrum was crossed by a large number of diffuse bands, at an average interval of about 20 A. These were unfortunately not sufficiently well differentiated from the continuous background for accurate measurements to be made. It is improbable that their presence can be traced to any impurity in the gases employed; and they were also observed in the flame of carbon monoxide burning alone in air.

Oxy Coal Gas Flame.

The explosion region of this flame exhibits only the λ 3883 head of the whole cyanogen spectrum, and that extremely faintly, though the hydrocarbon band Cη, with heads at λ 3872 and λ 3893, is strongly developed. The " ammonia " head at λ 3360 is quite distinct, being much stronger than the cyanogen head. The appearance of these two heads may almost certainly be attributed to the traces of nitrogen compounds inevitably present in coal-gas.

With a view to a further determination of the conditions affecting the development of the cyanogen bands, several nitrogen compounds were introduced in small quantity into the oxy-coal-gas flame, and the spectrum of the inner cone photographed. The compounds used were ammonia, nitro-ethane, and piperidine. The addition of each of these resulted in the appearance of the cyanogen bands at λ 3883 and λ 3590, quite strongly developed, while the " ammonia " band was also strengthened. These observations show that elementary nitrogen is probably inefficient in producing the cyanogen bands in the oxy-coal-gas flame, while any form of combined nitrogen is capable of producing them.

Conclusions.

1. In conjunction with previous existing evidence, the observations recorded above seem to leave no doubt that the production of the cyanogen bands is due to a carbon-nitrogen compound, and to neither element alone. A summary of the evidence available from the study of flame spectra is given.

Flames in which CN bands are developed.	Flames in which CN bands are absent.
1. Coal-gas-nitrous oxide.	1. Hydrogen-nitrous oxide.
2. Coal-gas-air (+ammonia, nitroethane or piperidine).	2. Hydrocarbon-oxygen flames in general.
3. Carbon monoxide-air and NH₃.	3. Ammonia-oxygen.
4. (CN)₂ and HCN-air.	4. Carbon monoxide-oxides of nitrogen.
5. Methylamine-air, and in the flames of other nitrogenous organic substances.	

It will be seen that in no case are the bands developed unless both carbon and nitrogen are present in the flame. Perhaps the clearest demonstration that carbon plays an essential part in the emission of these bands is afforded by the result of the addition of a trace of hydrocarbon to the nitrous oxide-hydrogen flame.

Evidence, from sources other than flame spectra, is not lacking. It is known, for example, that the cyanogen bands are not developed in vacuum tubes containing pure nitrogen and hydrogen, while the addition of traces of hydrocarbons, or of other carbon compounds, causes their appearance. The

bands are one of the most conspicuous features of the carbon arc in air, but are either absent from or only faintly visible in metallic arcs. Grotrian and Runge's explanation, which is based on the reducing powers of carbon relative to those of the metals, is difficult to uphold in view of the absence of the bands from the magnesium arc in air. That they do sometimes appear faintly in such metallic arcs is only to be expected, when the extreme difficulty of obtaining samples of metals free from traces of carbon is borne in mind. There is no doubt that Grotrian and Runge are correct in their statement that the presence of oxygen is unfavourable to the production of the bands, a fact which accounts for their detection in metallic arcs in nitrogen, when oxygen is excluded. This does not prove, however, that the bands are produced independently of the presence of carbon.

The evidence, by which Grotrian and Runge support their conclusion that the cyanogen bands are due to nitrogen alone, rests upon two assumptions :—

(i) That the nitrogen may be considered to be free from carbon when the Swan and other carbon bands are absent.

(ii) That if the cyanogen bands were due to a carbon complex, their intensity would be proportional to the amount of carbon present.

The first assumption is definitely disproved by the possibility of adding sufficient carbon to the nitrous oxide-hydrogen flame to cause the strong development of the cyanogen bands, while the remaining carbon bands cannot be detected. Hemsalech (loc. cit.) made a parallel observation with regard to the spectrum of the " red fringe " developed under an electrically heated graphite plate. The cyanogen head at $\lambda 3883$ was detected when the plate was heated to 2500° C., while the Swan bands only appeared at a temperature 500° C. higher.

It is clear that it is an easy matter to realise conditions under which the cyanogen bands can be developed independently of the rest of the carbon spectrum. The production of the cyanogen head at $\lambda 3883$ can, in fact, be made to yield the most delicate test for the presence of carbon.

This fact invalidates the conclusion drawn from Grotrian and Runge's demonstration of the inhibiting effect of oxygen on the appearance of the bands in the copper arc burning in nitrogen. The passage of the gas through pyrogallol (which was used as an oxygen absorbent), in the experiment they describe, might account for the development of the cyanogen bands, while the rest of the carbon bands would still remain invisible.

That the second assumption is also untenable without further experimental support was shown by the same observation with the nitrous oxide-hydrogen flame. The addition of a very small percentage of hydrocarbon to the hydrogen caused almost as intense a development of the bands

as did the complete replacement of hydrogen by coal-gas. Foley's observations (*loc. cit.*) are worth recalling in this connection. He found that the intensity of the cyanogen bands in the carbon arc bear little relation to the amount of nitrogen available. It may be noted also that Grotrian and Runge considered the "ammonia" band at λ 3360 to be part of the cyanogen spectrum; evidence based on a discussion of this band is obviously irrelevant.

Summary.

(i) Observations have been made of the spectra of the flames of a number of gases containing carbon, hydrogen, nitrogen, and oxygen.

(ii) The cyanogen bands are strongly developed in the coal-gas-nitrous oxide flame.

(iii) Evidence has been obtained that they are entirely absent from the hydrogen-nitrous oxide flame, if all traces of carbon are excluded, and it appears to follow that the presence of carbon is essential to their production.

(iv) The appearance of the cyanogen bands is, under appropriate conditions, a more delicate test for carbon than that of any of the other bands associated with that element. On the other hand, this spectrum is not necessarily developed when both carbon and nitrogen are present.

(v) The conclusion of Grotrian and Runge, that the cyanogen spectrum is to be attributed to nitrogen, is shown to rest on assumptions which are not confirmed in the present investigation.

(vi) The cyanogen spectrum provides a very delicate test for the presence of compounds of nitrogen admitted in the form of a gas to hydrocarbon flames burning in air, since elementary nitrogen does not appear, under ordinary circumstances, to be effective in producing cyanogen bands in such flames.

(vii) The intensity of the cyanogen bands, when carbon compounds are admitted to the hydrogen-nitrous oxide flame, bears no simple relation to the amount of carbon thus added.

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